SUPPLEMENTARY INFORMATION

Investigation of 19th and early 20th century Prussian blue production methods and their influence on the pigment composition and properties

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Recipe sources and original texts

Historical sources were studied using scans of the original books, accessed from the Internet Archive or Google Books. Original texts of all the replicated recipes are given below.

Recipe A: a direct method for soluble Prussian blue, by A. H. Church (1890) from Church, A. H. *The Chemistry of Paints and Painting*; Seeley and Co. Limited: London, 1890; pp. 188–189. Internet Archive, archive.org/details/gri_33125003356652 [1].

"Soluble Prussian Blue. — This is made by pouring a solution of ferric chloride or ferric nitrate into an excess of potassium ferrocyanide solution (yellow prussiate of potash), or by pouring ferrous sulphate solution into excess of potassium ferricyanide solution. The blue precipitate formed is washed with distilled water until the wash-water begins to acquire a blue tint. The composition of the pigment thus prepared is, when dry, represented by the formula $K_2Fe_2(CN)_{12}Fe_2$. It contains potassium, and is, in reality, a double ferrocyanide — a ' potassio-ferric ferrocyanide.' It is less stable than either of the other kinds of Prussian blue, while its solubility in water causes it to stain the paper

on which it is spread in water-colour painting. It should invariably be rejected by artists, although it must be owned that it works very smoothly both in water and in oil."

Recipe B: an indirect method for soluble Prussian blue, by J. Bersch (1893) from Bersch, J. *The Manufacture of Mineral and Lake Pigments, Containing Directions for the Manufacture of All Artificial Artists' and Painters' Colours, Enamel Colours, Soot and Metallic Pigments: A Text-Book for Manufacturers, Merchants, Artists and Painters*, 2nd ed.; Scott, Greenwood & Co.: London, 1901; pp. 197–198; translated by A. C. Wright. Internet Archive, archive.org/details/manufactureofmin00bersrich [2].

"The proportion of materials in which the least loss is involved is here given. Nine kilogrammes of green vitriol are dissolved in 100 litres of water, 15 kilogrammes of strong sulphuric acid are added, and then a solution of 15 kilogrammes of yellow prussiate in 100 litres of water. The solutions are kept in constant motion during the mixing. As soon as the decomposition is finished, without waiting for the precipitate to settle, steam is led in and 20 kilogrammes of nitric acid of 1.3298 specific gravity added in small portions. The heating by direct steam is continued until red vapours are no longer evolved from the liquid, which is a sign that the oxidation is finished."

The above text was used for replication of the recipe, but it is a 1901 translation of the original 2nd German edition from 1893. The text below is the German original, from Bersch, J. *Die Fabrikation Der Mineral- und Lackfarben, Enthaltend: Die Anleitung zur Darstellung aller künstlichen Maler- und Anstreicherfarben, der Email und Metallfarben; ein Handbuch für Fabrikanten, Farbwaarenhändler, Maler und Anstreicher*, 2nd ed.; A. Hartleben's Verlag: Wien, Pest, Leipzig, 1893; pp. 255–256. Google Books, books.google.nl/books?id=DG8QAwAAQBAJ [3].

„Ein Verhältniß der Stoffe, bei dem man den wenigsten Verlust an wirksamen Bestandtheilen erleidet, ist das nach stehend angegebene:

Man löst in 100 Liter Wasser 9 Kilogramm Eisenvitriol, fügt der Lösung 15 Kilogramm concentrirte Schwefelsäure zu und mischt sie mit einer Lösung von 10 Kilogramm gelbem Blutlaugensalz in 100 Liter Wasser. Die Lösungen werden während des Zusammengießens in steter Bewegung erhalten und sobald man annehmen kann, daß die Zersetzung erfolgt sei, läßt man, ohne zu warten, daß sich der Niederschlag zu Boden senke, einen Dampfstrom durch die Flüssigkeit gehen und gießt in kleinen Partien 20 Kilogramm Salpetersäure vom specifischen Gewichte 1.3298 hinzu. Man fährt mit dem Erhitzen durch directen Dampf so lange fort, bis aus der Flüssigkeit keine rothen Dämpfe mehr entweichen, was ein Beweis dafür ist, daß die Oxydation beendet ist."

Recipe C: an indirect method for soluble Prussian blue, by J. Bersch (1893) from Bersch, J. *The Manufacture of Mineral and Lake Pigments, Containing Directions for the Manufacture of All Artificial Artists' and Painters' Colours, Enamel Colours, Soot and Metallic Pigments: A Text-Book for Manufacturers, Merchants, Artists and Painters*, 2nd ed.; Scott, Greenwood & Co.: London, 1901; p. 198; translated by A. C. Wright. Internet Archive, archive.org/details/manufactureofmin00bersrich [2].

"In the process recommended by Gentele 109 parts of yellow prussiate are used to 20 parts of green vitriol, each dissolved in much water. The precipitate is heated for a short time with 51 parts of nitric acid of 1.2285 specific gravity and 16 parts of sulphuric acid. The mixture is allowed to stand for several days to complete the oxidation before the precipitate is separated from the liquid."

The above text was used for replication of the recipe, but it is a 1901 translation of the original 2nd German edition from 1893. The text below is the German original, from Bersch, J. *Die Fabrikation Der Mineral- und Lackfarben, Enthaltend: Die Anleitung zur Darstellung aller künstlichen Maler- und Anstreicherfarben, der Email und Metallfarben; ein Handbuch für Fabrikanten, Farbwaarenhändler, Maler und Anstreicher*, 2nd ed.; A. Hartleben's Verlag: Wien, Pest, Leipzig, 1893; p. 256. Google Books, books.google.nl/books?id=DG8QAwAAQBAJ [3].

„Nach dem von Gentele empfohlenen Verfahren wendet man auf 109 Theile Blutlaugensalz 20 Theile Eisenvitriol an, welche in viel Wasser gelöst zusammengebracht werden. Der Niederschlag wird mit 51 Theilen Salpetersäure von 1.2285 (27 °Be.) und 16 Theilen Schwefelsäure durch kurze Zeit erhitzt, worauf man das Ganze zur Vollendung der Oxydation durch einige Tage stehen läßt, bevor man den Niederschlag von der Flüssigkeit trennt."

Recipe D: a direct method for soluble Prussian blue, by J. Bersch (1893) from Bersch, J. *The Manufacture of Mineral and Lake Pigments, Containing Directions for the Manufacture of All Artificial Artists' and Painters' Colours, Enamel Colours, Soot and Metallic Pigments: A Text-Book for Manufacturers, Merchants, Artists and Painters*, 2nd ed.; Scott, Greenwood & Co.: London, 1901; p. 201; translated by A. C. Wright. Internet Archive, archive.org/details/manufactureofmin00bersrich [2].

“Brücke gives the following method: a solution is prepared of 217 grammes of yellow prussiate in 11 kilogrammes of water. Another solution contains 100 grammes of ferric chloride in 1 litre, 1 litre of which is mixed with 2 litres of a saturated solution of Glauber's salt and the mixture added to the prussiate solution so long as a blue precipitate forms. The Glauber's salt plays no part in the formation of the colour; it is added to prevent the solution of the precipitate, which is insoluble in salt solutions. The precipitate is brought on to a filter and washed with water until the washings begin to be blue, which is a sign that the salts have been almost completely removed. The precipitate cannot be further washed without the loss of a large quantity which would be dissolved by the water; without further washing it is slowly dried in the air.”

The above text was used for replication of the recipe, but it is a 1901 translation of the original 2nd German edition from 1893. The text below is the German original, from Bersch, J. *Die Fabrikation Der Mineral- und Lackfarben, Enthaltend: Die Anleitung zur Darstellung aller künstlichen Maler- und Anstreicherfarben, der Email und Metallfarben; ein Handbuch für Fabrikanten, Farbwaarenhändler, Maler und Anstreicher*, 2nd ed.; A. Hartleben’s Verlag: Wien, Pest, Leipzig, 1893; p. 260. Google Books, books.google.nl/books?id=DG8QAwAAQBAJ [3].

„Nach der von Brücke angegebenen Methode erhält man ein sehr leicht lösliches Berlinerblau auf die Weife, daß man sich die nachstehend angegebenen Lösungen bereitet: die eine Lösung wird dargestellt aus 11 Kilogramm Wasser und 2170 Gramm Blutlaugensalz; die andere enthält 100 Gramm Eisenchlorid in einem Liter Flüssigkeit; man mischt ein Liter dieser Lösung mit dem doppelten Volumen einer gesättigten Lösung von Glaubersalz in Wasser und fügt von dieser Lösung so lange zu der Lösung des Blutlaugensalzes, als noch ein blauer Niederschlag entsteht.

Der Zusatz des Glaubersalzes ist in Bezug auf die Entstehung der Farbe selbst vollkommen indifferent und hat nur den Zweck, die Auflösung des Niederschlages, der, wie schon früher erwähnt wurde, in Salzlösungen unlöslich ist, zu verhindern.

Der Niederschlag wird auf ein Filter gebracht und so lange mit Wasser gewaschen, bis sich das Waschwasser blau zu färben anfängt, was ein Zeichen dafür ist, daß die Salze zum größten Theile entfernt sind. Man kann nun den Niederschlag nicht mehr weiter mit Wasser behandeln, ohne eine große Menge desselben durch Auflösung im Wasser zu verlieren; man unterbricht daher das weitere Waschen und trocknet den in den Filtern zurückbleibenden Niederschlag allmälig an der Luft ganz aus.“

Recipe E: an 18th century method for Prussian blue, by J. Woodward (1724) translation from Powell, H. M. The Beginnings of Co-Ordination Chemistry. *Proc. Chem. Soc.* **1959**, 73–108 [4].

"Take 4 oz. of crude tartar and 4 oz. of dried crude nitre; powder them minutely and mix. Detonate them with charcoal, and you then have 4 oz. of extemporaneous alkali. While this salt is still hot it is finely powdered and 4 oz. of well-dried and finely powdered ox blood is added. These well-mixed components are placed in a crucible so that it is two-thirds filled. After it has been covered with a lid it is put on a fire and the crucible is piled round with coals so that it gradually begins to glow and the material takes fire and begins to burn without any violent outburst. The material is kept in this degree of fire until the flame and eruption slacken. The fire is then increased until the substance glows intensely and little further flame emanates from the crucible. Then remove the crucible from the fire and grind the material gently in a mortar; have ready 2 pints of boiling fresh water into which the material is thrown while still glowing and boil for the space of half an hour. The decoction is passed through a piece of linen and the remaining black material, on to which a further portion of water is poured, is once more placed on the fire, boiled, and filtered. This procedure should be continued until the saltiness and all bitterness have been washed out and the water remains insipid. Well press out all the liquors remaining in the linen and the material and when you have collected them all together, place again on the fire and evaporate down to 3½ pints and keep for later use. (No. 1). Then take 1 oz. of green vitriol, calcined gently to whiteness, and dissolve it in 6 oz. of fresh water; filter through paper and call this No. 2. Then take 8 oz. of crude alum. Treat it with 2 pints of boiling water until complete dissolution of the alum and when this has been done, add it to the solution of vitriol No. 2 which is taken, boiling, from the fire, put into a pot of sufficient capacity and combined with the well boiling lixivium No. 1, previously set apart. There is a great effervescence of the contents and a green or greenish-blue colour appears. The liquid is poured alternately from one vessel to another during the effervescence, until it stops; then let it stand. It is then transferred to a piece of linen so that the liquors may flow through and the coloured substance remain on the linen. When no further water drips through it is removed from the linen with the aid of a wooden spatula into a fresh, smaller pot. Pour on to it 2 or 3 oz. of spirit of common salt and at once there appears a most beautiful blue colour. All is well stirred and allowed to settle overnight. Then a large quantity of fresh water is added and stirred with a spatula. After the material has settled the water is decanted and a fresh lot of water is poured over it, and this operation is repeated until all bitterness has been washed away and the water which flows out is insipid. When this has been completed, transfer the intensely blue precipitate to a taut piece of linen so that the water may gradually drain away. The pigment is dried in a gentle heat, and is then ready for use.

N.B.-In this procedure the calcination is of great importance because the sea-blue colour and the hidden sky-blue arise according as the calcination of the dried blood with the alkali is light,

medium, or strong, and hence there is a diversity of colour. The well-boiling lixivia are to be mixed one with the other in the most rapid manner."

The above text was used for replication of the recipe, but it is a 1959 translation of the original Latin publication from Woodward, J. Praeparatio Caerulei Prussiaci Ex Germania Missa. *Philos. Trans*. **1724**, *33*, 15–17 [5]. The original Latin text is not included here.

Recipe F: an 18th century method for Prussian blue, by R. Dossie (1758) from Dossie, R. *Handmaid to the Arts*, Volume I.; J. Nourse: London, 1758; pp. 78–80. Internet Archive, archive.org/details/handmaidtoartsb00dossgoog [6].

"The Prussian blue may be prepared in perfection by the following process.

Take of blood any quantity; and evaporate it to perfect dryness. Of this dry blood, powdered, take six pounds, and of the best pearl-ashes two pounds: mix them well together in a glass or stone mortar; and then put the mixt matter into large crucibles or earthen-pots; and calcine it in the furnace described, p.22; the top of the crucible or pot being covered with a tile, or other such convenient thing, but no luted. The calcination should be continued, so long as any flame appears to issue from the matter; or rather till it become very slender and blue; for if the fire be very strong, a small flame would arise for a very long time. When the matter has been sufficiently calcined, take the vessels which contain it out of the fire; and, as quickly as possible, throw it into two or three gallons of water; and, as it soaks there, break it with a wooden spatula, that no lumps may remain. Put it then in a proper tin-vessel, and boil it for the space of three quarters of an hour or more; and filter it while hot through paper in the tin cullenders described, p.27; and pass some water through the filter when it is run dry, to wash out the remainder of the lixivium of the blood and pearl-ashes; the earth remaining in the filter may be then thrown away. In the mean time, dissolve of clean alum four pounds, and of green vitriol or copperas two pounds, in three gallons of water. Add this solution gradually to the filtered lixivium, so long as any effervescence appear to arise on the mixture; but, when no ebullition or ferment follows the admixture, cease to put in more. Let the mixture then stand at rest, and a green powder will be precipitated: from which, when it has thoroughly subsided, the clear part of the fluid must be poured off, and fresh water put in its place, and stirred well about with the green powder: and, after a proper time of settling, poured off like the first. Take then of spirit of salt double the weight of the green vitriol which was contained in the quantity of solution of vitriol and alum added to the lixivium, which will soon turn the green matter to a blue colour; and, after some time, add a proper quantity of water, and wash the colour in the same manner, as has

been directed for lake, &c.; and when properly washed, proceed in the same manner to dry it in lumps of convenient size."

Recipe G. an ion exchange method for insoluble Prussian, by A. H. Church (1890) from Church, A. H. *The Chemistry of Paints and Painting*; Seeley and Co. Limited: London, 1890; p. 189. Internet Archive, https://archive.org/details/gri_33125003356652 [1].

"Insoluble Prussian Blue may be prepared by boiling No. I. (the soluble kind) with a solution of ferric chloride, by mixing solutions of ferrocyanic acid and ferric chloride, by pouring potassium ferrocyanide solution into an excess of a solution of ferric chloride, or of ferric nitrate, and heating the mixture for some time, or by precipitating a watery solution of Blue No. I. with an excess of either of the abovenamed iron salts. It may also be obtained by oxidizing Turnbull's blue (No. III.) with chlorine water or nitric acid. The chemical composition of this pigment is very complex, the simplest empirical formula for it being $Fe_7(CN)_{18}$: it will be seen that it contains no potassium. It always contains some combined water, which cannot be driven off by heat without decomposition of the salt. This blue is more permanent than No. I."

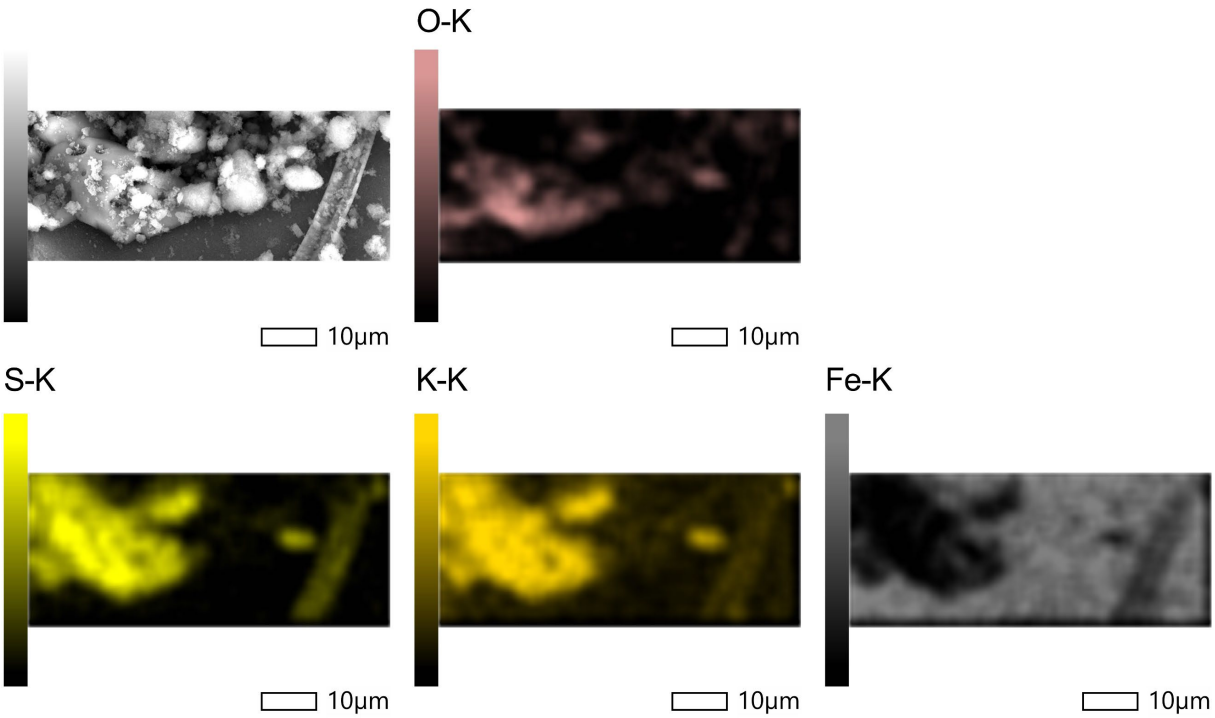

Figure S1. *SEM image and corresponding net EDX maps of oxygen, sulphur, potassium and iron showing the presence of a potassium sulphate needle and larger particle in Prussian blue prepared according to recipe B.*

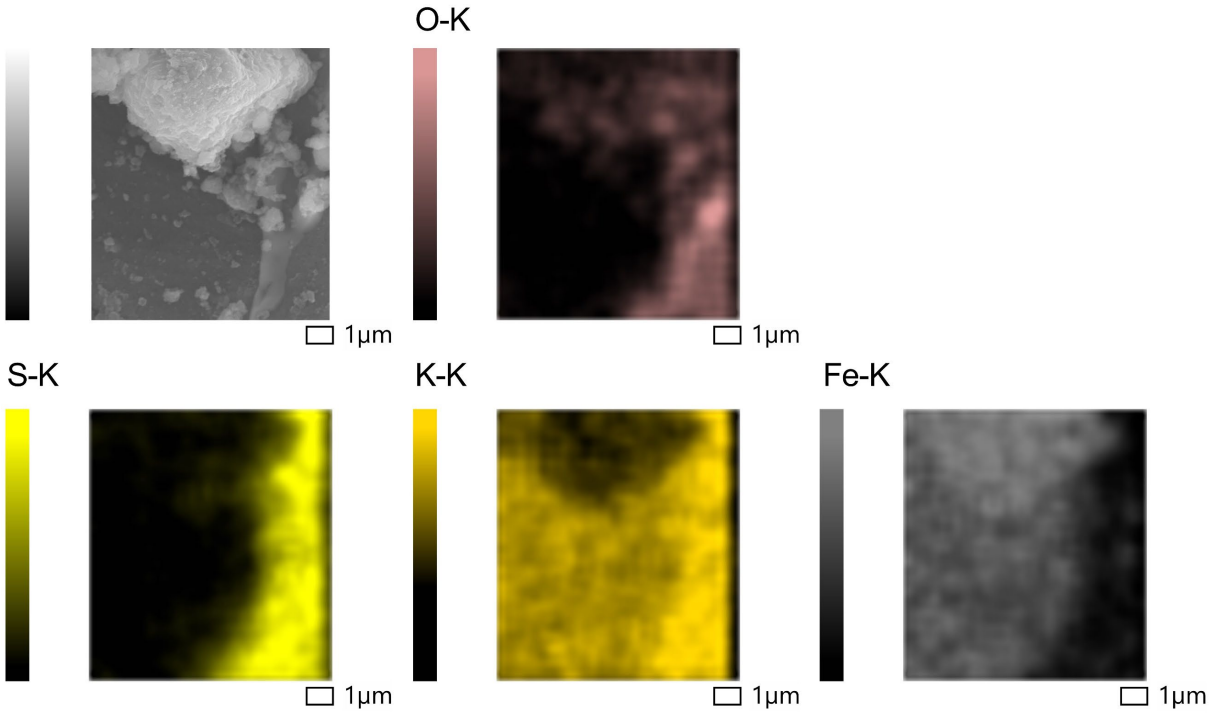

Figure S2. *SEM image and corresponding net EDX maps of oxygen, sulphur, potassium and iron showing the presence of potassium sulphate in Prussian blue prepared according to recipe C.*

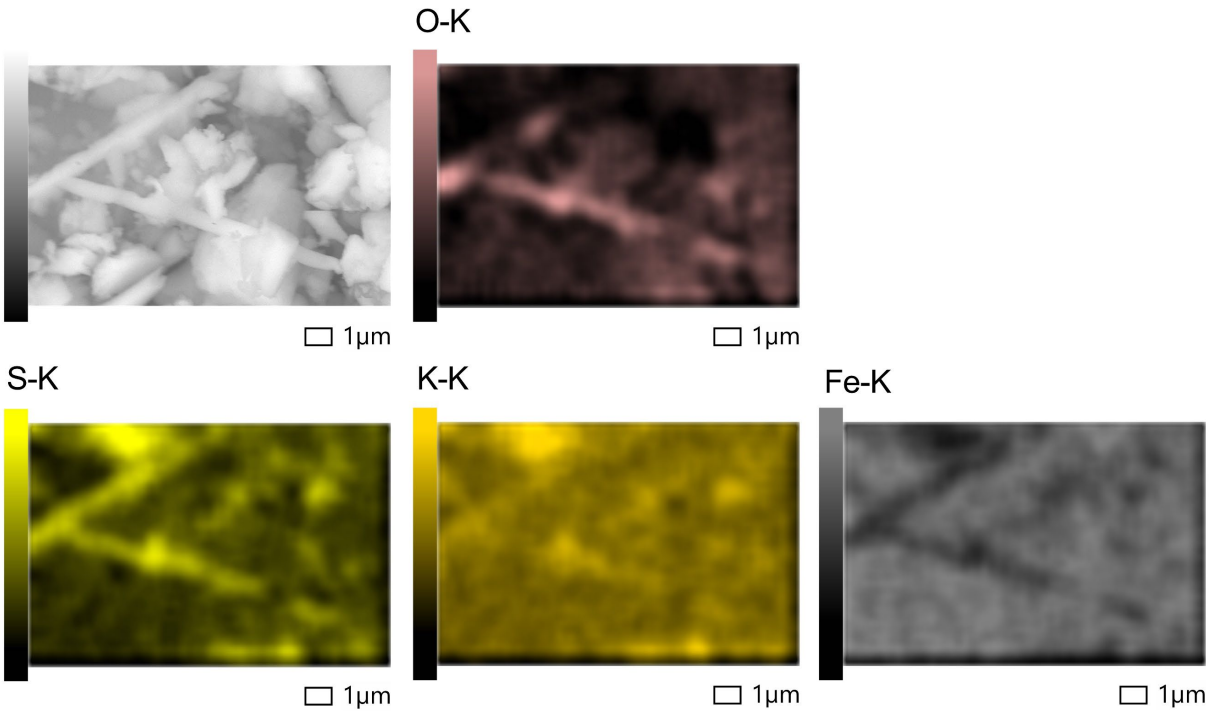

Figure S3. *SEM image and corresponding net EDX maps of oxygen, sulphur, potassium and iron showing the presence of potassium sulphate needles in Prussian blue prepared according to recipe D.*

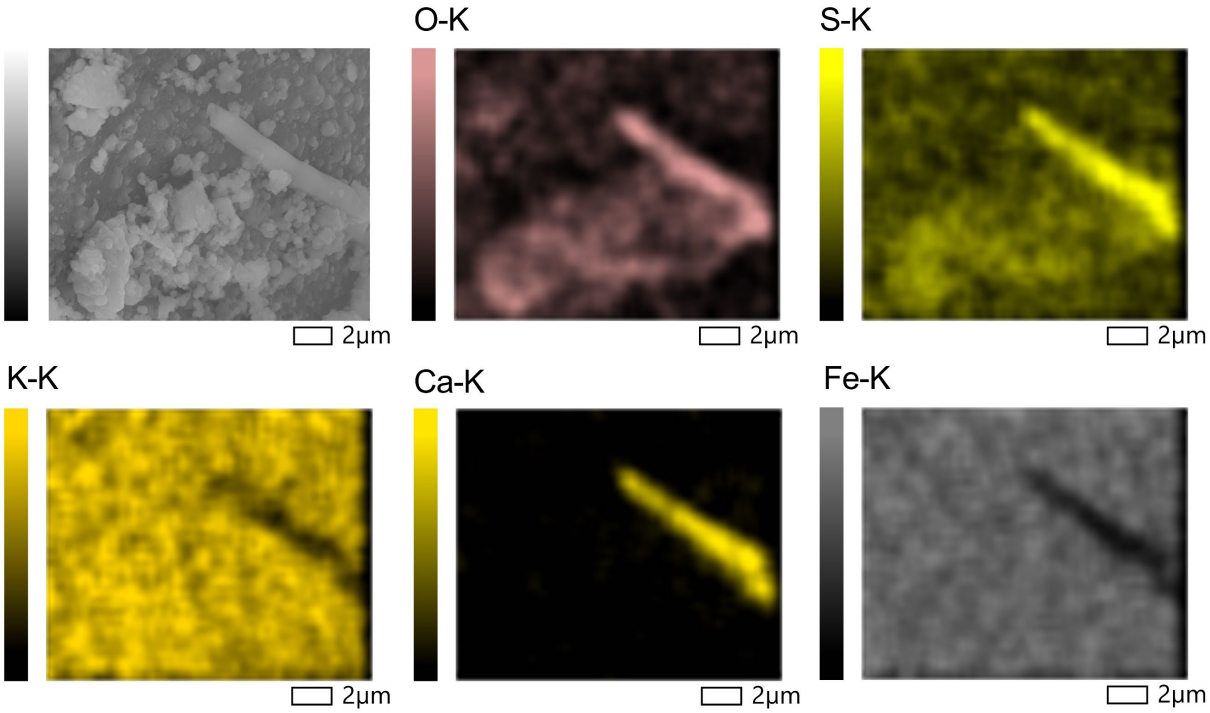

Figure S4. *SEM image and corresponding net EDX maps of oxygen, sulphur, potassium, calcium and iron showing the presence of calcium sulphate needle in Prussian blue prepared according to recipe F.*

References

[1] Church AH. The chemistry of paints and painting. London: Seeley and Co. Limited; 1890.

[2] Bersch J. The manufacture of mineral and lake pigments. 2nd ed. London: Scott, Greenwood & Co.; 1901.

[3] Bersch J. Die Fabrikation der Mineral- und Lackfarben. 2nd ed. Wien, Pest, Leipzig: A. Hartleben's Verlag; 1893.

[4] Powell HM. The beginnings of co-ordination chemistry. Proceedings of the Chemical Society 1959:73–108. https://doi.org/10.1039/ps9590000073.

[5] Woodward J. Praeparatio Caerulei Prussiaci Ex Germania Missa. Philos Trans 1724;33:15–7.

[6] Robert Dossie. The Handmaid to the Arts. Volume I. London: J. Nourse; 1758.